In-situ identification and absolute separation of small molecules by single crystal X-ray diffraction in metal-organic framework

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1. Materials and Methods

Commercially available reagents were used throughout without further purification and azobenzene-3,3'-dicarboxylic acid (H_2AzDC) was synthesized according to the literature method. All materials were used without further purification.

Elemental analyses for C, H, and N were performed with a PerkineElmer 2400 Series II element analyzer. Thermogravimetric analysis (TG) was performed by a TGA Q500 thermal analysis system. All TGA experiments were performed under a N_2 atmosphere from 30 to 1200 °C at a rate of 10 °C/min. Before carring out X-ray powder diffraction, the fresh crystal samples after naturally drying for one week were grinded to give an even powder samples. Then these powder samples were collected by a Bruker AXSD8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα (λ = 1.5406 Å). The simulated PXRD data was obtained from single crystal data by Mercury 1.4. The gas sorption isotherms were collected on a Belsorp-max. Ultra pure CH_3OH, C_2H_5OH, and C_3H_7OH of GC grade were used in the adsorption measurement. To maintain the experimental temperature 298 K was using a close air-condition system and traced using a thermometer.

2. Experimental Procedures

2.1The syntheses of 1-4. The mixture of adding methanol (2ml) or ethanol (2ml) or propanol (2ml) or DMF (2ml) into a DMF solution (3ml) containing $MnCl_2 \cdot 4H_2O$

(0.2mmol), H$_2$AzDC (azobenzene-3,3′-dicarboxylic acid, 0.2mmol), was sealed in a Teflon reactor, and further heated at a rate of 1 °C min^{-1} to 120°C, and kept at that temperature for 25 hours, and then it was cooled to room temperature at a rate of 3°C h^{-1}. Subsequently, the jacinth block crystals were isolated from the solution by filtration and then dried naturally for one week, obtaining in 90%-**1**, 88%-**2**, 89%-**3**, 86%-**4**, yield based on Mn(II), respectively. EA (%): For **1**,calc. C 50.72, H 4.56, N 10.56; exp. C 50.70, H 4.58, N 10.55. For **2:** calc. 51.44, H 4.67, N 10.34; exp. C 51.46, H 4.65, N 10.36. For **3:** calc. C 52.14, H 4.96, N 10.13; exp. C 52.16, H 4.95, N 10.12. For **4:** calc. C 51.47, H 4.75, N 12.00; exp. C 51.45, H 4.77, N 12.01.

Table S1. The crystallography data for **1-4**.

Compounds	**1**	**2**	**3**	**4**
Formula	$C_{56}H_{58}Mn_3N_{10}O_{18}$	$C_{58}H_{64}Mn_3N_{10}O_{18}$	$C_{60}H_{68}Mn_3N_{10}O_{18}$	$C_{60}H_{66}Mn_3N_{12}O_{17.5}$
Formula weight	1323.94	1354.01	1382.06	1400.07
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1	P-1
a /Å	11.248(2)	11.2155(19)	11.3694(7)	11.5248(6)
b /Å	12.241(2)	12.436(2)	12.4390(7)	15.4562(9)
c /Å	12.431(3)	12.440(2)	12.4649(8)	18.8105(11)
α /°	102.219(6)	91.252(8)	102.276(3)	91.181(3)
β /°	92.044(7)	91.252(8)	106.182(9)	105.699(4)
γ/°	109.964(6)	110.743(8)	92.234(3)	107.518(3)
Volume (Å^3)	1561.4(5)	1574.8(5)	1603.84(17)	3153.7(3)
Z	1	1	1	2
Dc/(g cm^{-3})	1.408	1.428	1.431	1.474
F(000)	683	701	717	1450
Reflections collected/unique	21636/5464	21589/5538	20291/5620	37138/10942
GOF on F^2	1.064	1.046	1.131	1.058
Final R indices [I>2sigma(I)]	R_1=0.0519, wR_2=0.1488	R_1= 0.0374, wR_2= 0.1029	R_1=0.0560, wR2=0.1288	R_1=0.0892, wR_2=0.2335
R indices (all data)	R_1=0.0595, wR_2=0.1580	R1=0.0427, wR_2= 0.1088	R_1=0.0674, wR_2=0.1395	R_1=0.1276, wR_2=0.2719
CCDC number	1475313	1475314	1475315	1475316

3. Crystal structure of compounds 2, 3 and 4

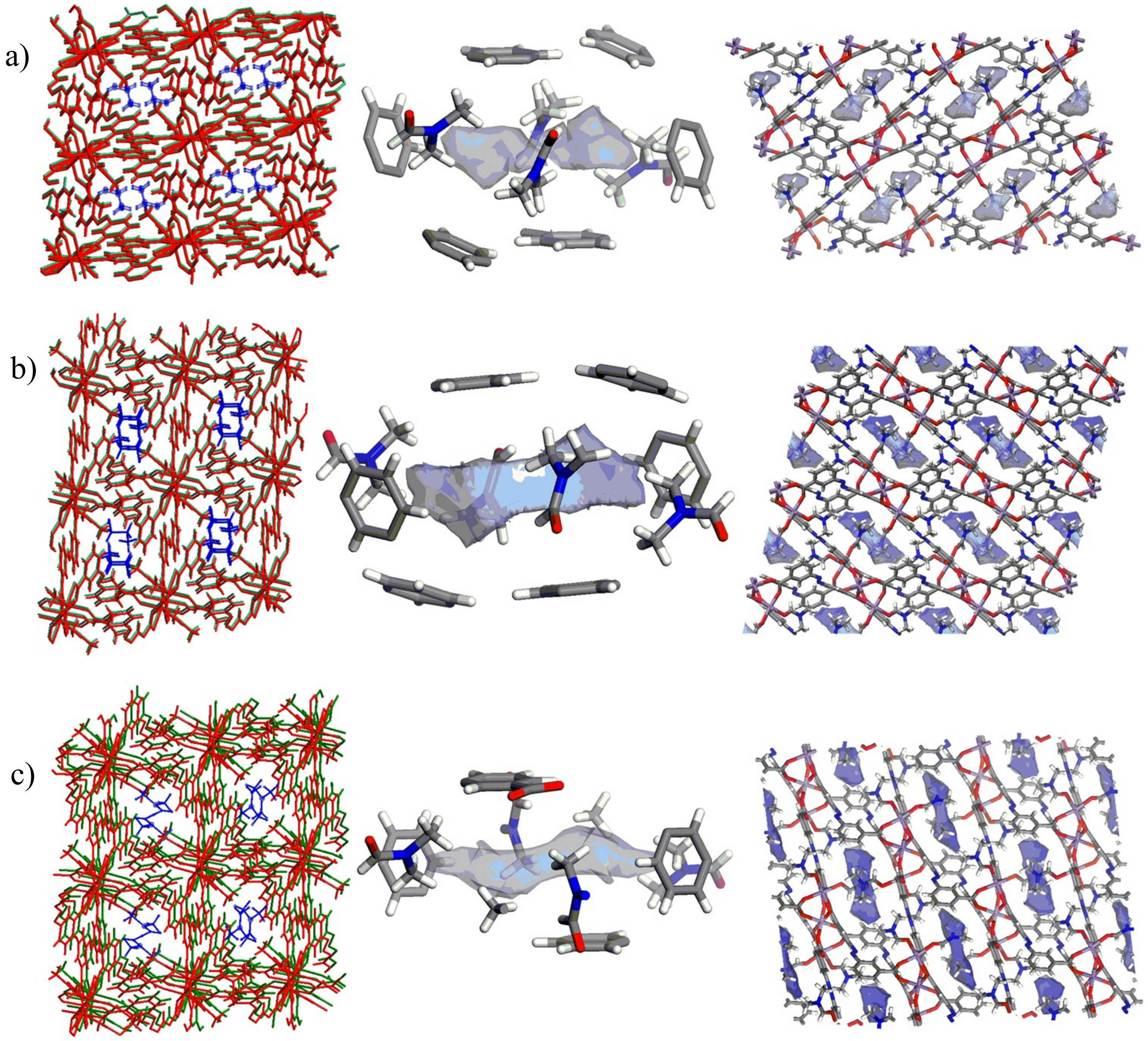

Fig. S1 View of the framework of compounds 2 (a), 3 (b), and 4 (c) and their inclusions.

4. TG diagram of compounds 1-4.

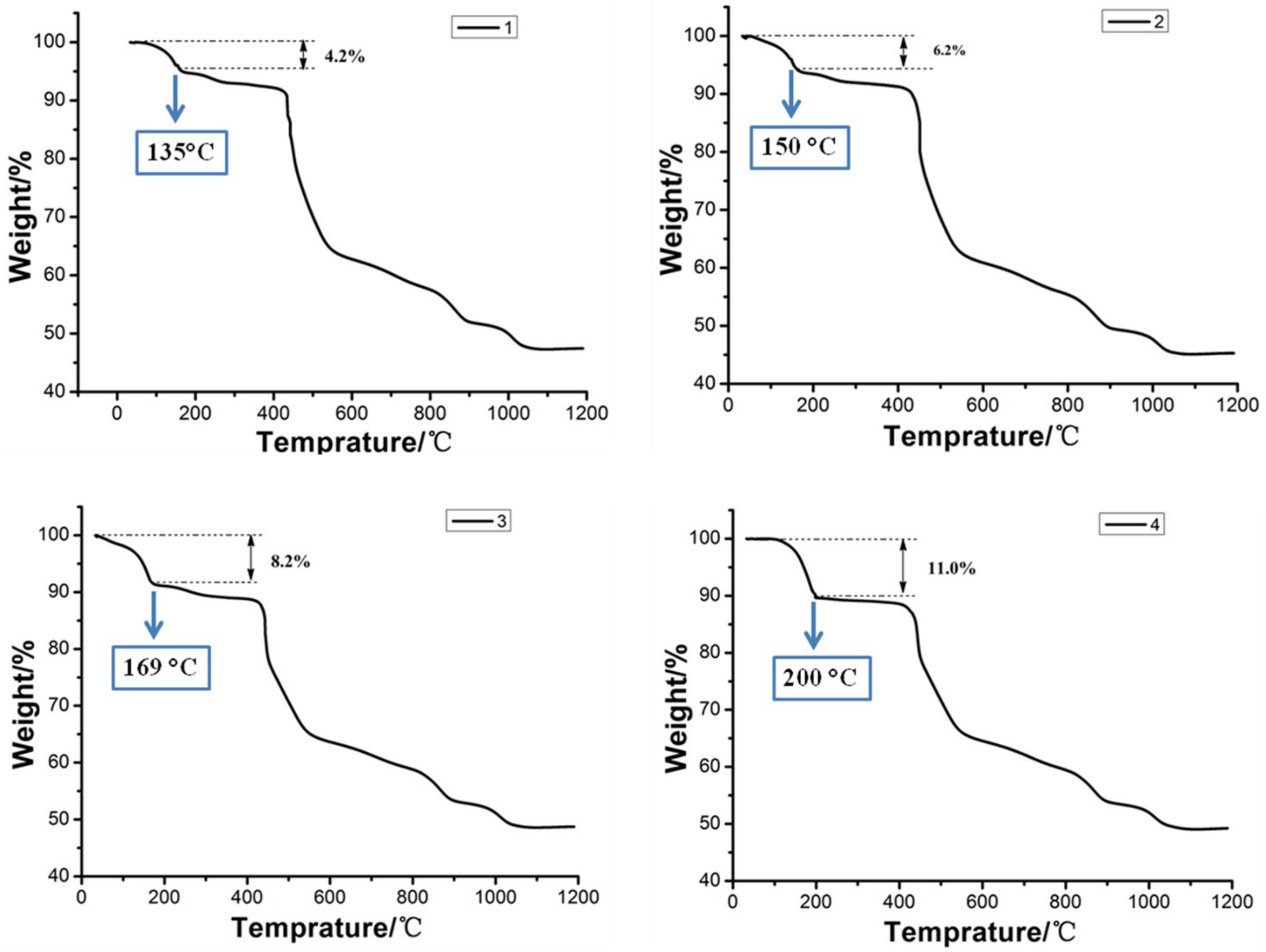

Fig. S2 The TG plots of compounds **1**-**4**.

5. Powder XRD patterns of compounds 1-4.

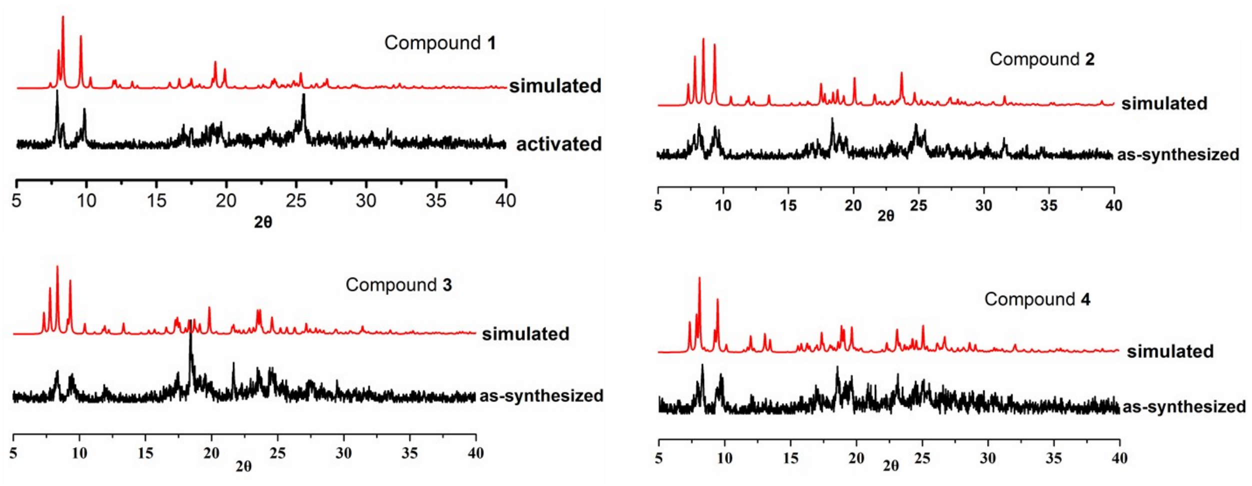

Fig. S3 The experimental and simulated PXRD patterns of compounds **1**-**4**. See from the crystal structure, it is clear that compounds **1**-**4** are isostructural. However, see from the crystal data as shown in Table S1, some differences such as increase in the unit volume are observed among comounds **1**-**3**, which, in conjunction with the inclusion of different solvents molecules, may result in somewhat difference in the PXRD patterns. As for compound **4**, the difference in PXRD pattern is mainly due to the distinct crystal data, relatively to that observed in compounds **1**-**3**.